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14. ABSTRACT

The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.

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POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #1

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1 Summary

Following a literature search and refinement of the research plan, we held our internal kickoff meeting. We reviewed the statement of work, and outlined tasks and methods in more detail than found in the proposal. We successfully grew hollow zinc tubes from a gold electrode. Plating conditions must be adjusted to form thicker walls, however. We were also successful in microencapsulating uncured polyurethane resin in a hard polyurethane shell using an emulsion technique. 45 g were made in a single batch, demonstrating that scale-up is relatively straightforward.

2 Project Goals and Objectives

The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.

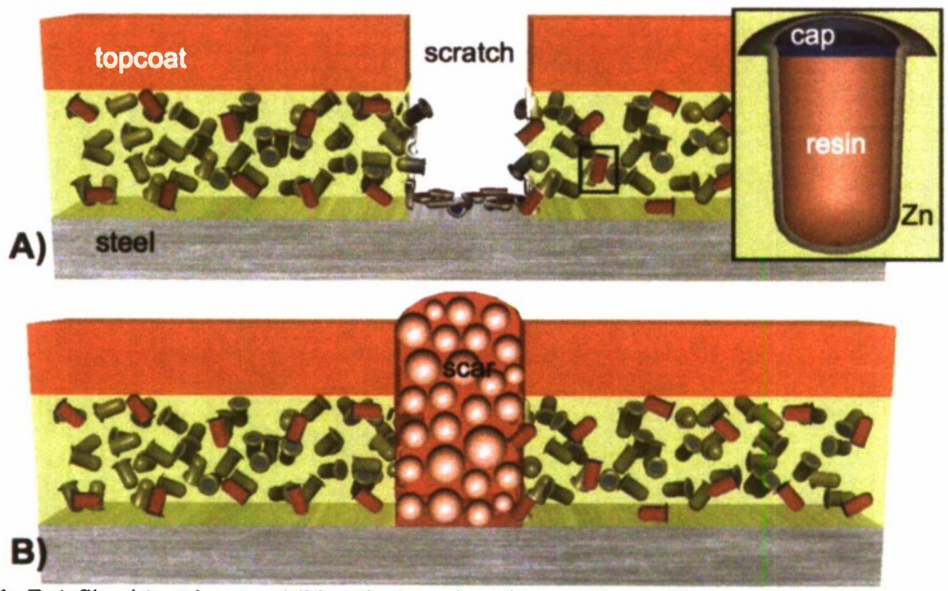

Figure 1: *Polyfibroblast is an additive that works with existing military grade primers to impart self-healing properties and galvanic protection. It consists of a moisture-cured polyurethane-urea that is microencapsulated in a hard zinc shell.*

The first two tasks are to choose a suitable polyurethane formulation, and to work out a method for microencapsulating uncured MCPU resin in a zinc shell. The initial focus of the polyurethane downselect is to determine which properties are most important for processability. Once we identify a subset of resins that are amenable to microencapsulation, we will shift our focus to the end-use properties, such as adhesion, shelf life, and water resistance. The search for a zinc capsule protocol centers initially around the growth of suitably sized, shaped, and durable structures. The focus will then shift towards scalability once we can reproducibly form capsules that serve the technological goals of this project.

3 Key Accomplishments

3.1 Detailed Planning and Kickoff Meeting

To stay updated on the latest developments in the technology relevant to this program, the first week was devoted to a thorough literature search. The search primarily focused on recent advances in electrochemical deposition of metals on polymers, polyurethane microencapsulation, and self-healing materials. These findings were then used to map out sample preparation protocols for each part of this project.

At the kickoff meeting, all team members were briefed on the statement of work and deliverables. In short, we will spend the first 6 months developing methods for making microencapsulated MCPU of the right size, shape, and quantity. The second 6 months will be spent on performance testing and refinement. For the earlier set of tasks, we have divided our members into a pair of teams: one team lead by Rengaswamy Srinivasan will focus on electrochemical preparation methods, the other team lead by Alan Becknell will focus on organic chemical preparation methods.

3.2 Preparation of Hollow Zinc Microtubes

3.2.1 Zinc microtube preparation on gold metallized membrane

A track ethched nucleopore© polycarbonate membrane (25 mm diameter, 10 μm thickness, 5 μm diamater pores) had one face metalized with 0.4 μm of gold via vapor phase deposition. This membrane was immersed into an aqueous zinc plating solution composed of 0.44 M zinc oxide and 10 M postassium hydroxide. The electrodeposition was carried out using a mercury/mercury oxide reference electrode and a standard platinum counter electrode. A voltage of -1.44 V was used to deposit the zinc and -0.12 C of metal was deposited into the pores.

The resulting tubes were hollow, as desired. However, the side-walls were generally incomplete. We also observed that the zinc plating was slightly asymmetric. By our calculations, the target thickness should have been on the order of 0.1 μm.

3.2.2 Zinc microtube preparation on composite gold and nickel metallized membrane

A track ethched nucleopore© polycarbonate membrane (25 mm diameter, 10 μm thickness, 5 μm diamater pores) had one face metalized with top layer consisting of 0.04 μm of nickel (this layer was in contact with the polymer membrane) and bottom layer consisting of 0.4 μm of gold via vapor phase deposition. This membrane was immersed into an aqueous zinc plating solution composed of 0.44 M zinc oxide and 10 M postassium hydroxide. The electrodeposition was carried out using a mercury/mercury oxide reference electrode and a standard platinum counter electrode. Voltages of -1.44 V and -0.6 V were used to deposit the zinc and -0.2 C of metal was deposited into the pores.

Some images of the microtubes are shown below. Note that they measure approximately 5 μm in diameter and 10 μm tall. The tubes formed on the gold electrode were slightly more complete and uniform than those formed on nickel. Moreover, the two were very similar. Observe how the top and bottom of the tubes are open. Since previous generations of this technology all involved solid metal wires, we were unaware that the metal electrode did not span the open pores. Furthermore, previous sample preparations focused on nanoscale pores, which may, in fact, be covered over by the metal electrode during vapor phase deposition. We do not anticipate that this surprising result will significantly complicate our overall technology development plan; forming one cap is no more difficult than forming two. The additional open end may actually make it easier to fill the tubes with resin.

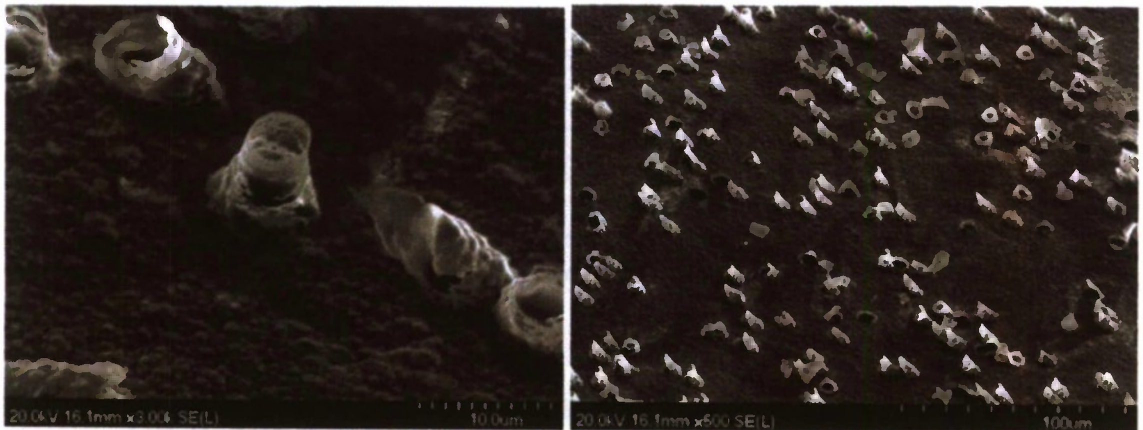

Figure 2: *Hollow zinc microtubes electroplated upon a gold electrode using a track-etched polycarbonate membrane as a template. The tubes are shown after the membrane is removed with chloroform.*

3.3 Preparation of Polyurethane Microcapsules

One of the processing steps outlined in the proposal involved the formation of a polyurethane skin layer as a cap to close the open end of the zinc tube. The need to form this skin layer has lead to exploration of polyurethane microencapsulation techniques employed widely by the perfume and pesticide industries. Due to the fact that this process is basically an interfacial polymerization performed in an oil-in-water emulsion, it holds great potential for scaling up while keeping costs low. Our initial attempts were inspired by a recent paper from the Sottos group at UIUC that was released in November. The recipe included an oil phase consisting of 10.7 g toluene diisocyanate prepolymer, 14.75 g chlorobenzene, 35 g isophoronediisocyanate. The aqueous phase included 110 ml water, 16.6 g gum Arabica, and 11.43 g 1,4-butanediol. After 45 min of stirring at 70 °C, we produced 100 μm microcapsules shown below.

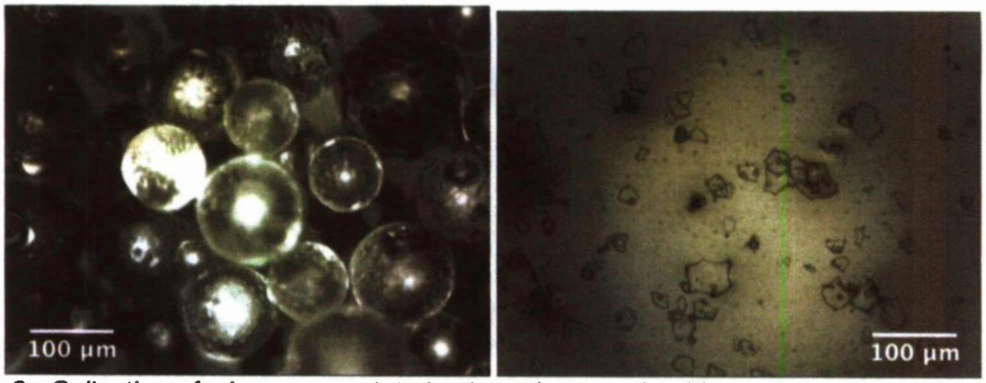

Figure 3: *Collection of microencapsulated polyurethane resin. The average size of the capsules is approximately 100 μm in diameter (left). While the skin thickness has not yet been characterized, rupture of the microcapsules has shown it to be only a small fraction of the diameter (right). The dimples on the skin layer are likely the product of volume loss due to thermal contraction and/or the evaporation of chlorobenzene after the skin layer has formed.*

The microcapsules shown in Figure 3 were stored in water for 5 days before taking that pair of micrographs. The thin shards of polyurethane that remained after ultrasonification demonstrate that the skin layer formed by this reaction is an effective moisture barrier. This result is promising given the concerns that the microencapsulated MCPU would have a limited shelf life. The shelf-life is expected to improve even further once the zinc outer shell is added and the microcapsules are embedded within a cured primer.

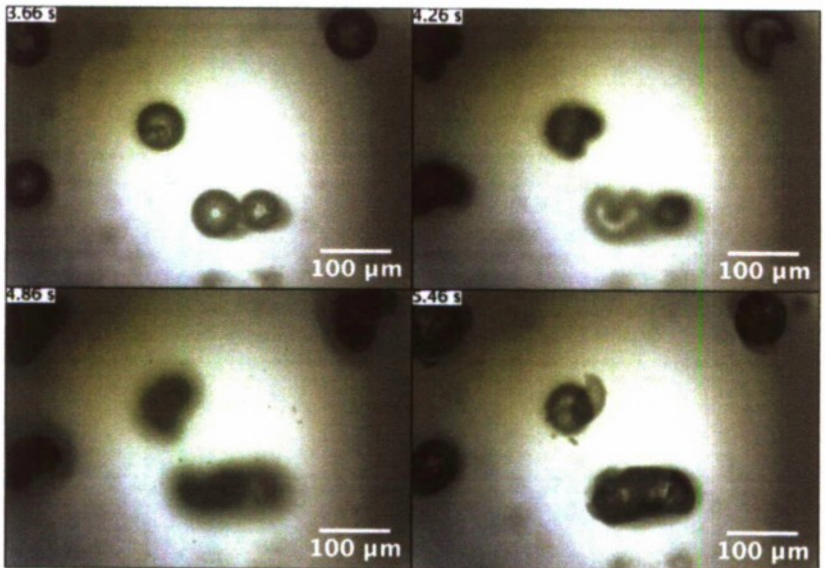

Figure 4: *A montage showing the microcapsules being squeezed by a cover slip pressing down on a glass slide.*

Characterization of the percentage of uncured MCPU has not yet been performed. However, we have been able to demonstrate the ability of the microcapsules to release MCPU upon rupture. Figure 4 shows a series of stills from a movie where the microcapsules are crushed between a glass slide and coverslip. Note how the MCPU not only ejects from the spheres, but that it also wets the upper coverslip fairly well.

3.4 Electroless Zinc Deposition

Electroless zinc deposition is an attractive method in this project since it eliminates the need for immobilization of the microstructures upon an electrode. It can be particularly useful in the case of the microcapsules described in the previous section. Also performed in aqueous solutions, it may be possible to perform the encapsulation and zinc deposition in a single step.

Initial attempts at electroless zinc deposition have not yet been successful. The initial recipe has been adapted from a protocol developed for nickel-zinc alloys. We prepared our plating solution by mixing 0.2 g zinc sulfate heptahydrate, 0.85 g sodium citrate, 0.5 g ammonium chloride, 0.2 g sodium hypophosphite, and 10 ml water adjusted to a pH of 10.5 with sodium hydroxide. After heating to 85 °C for 6 hours, zinc oxide precipitated from solution. It was noted that the pH had dropped from 10.5 to 6 during the heating cycle. The solution was not buffered.

4 Next Steps

4.1 Electrochemical Route

To overcome the issue of incomplete tube formation, we plan to increase our target thickness to 0.5 mm to see if continuous zinc walls are achievable. Although this early result was somewhat disappointing, we are very pleased with the preservation of these delicate structures. The final step of the sample preparation is to dissolve the polycarbonate membrane with chloroform. Despite possible swelling of the membrane, we saw little evidence of damage to any of the microtubes. This observation is especially impressive given that the wall thickness is probably only a few nanometers at points.

4.2 Emulsion Route

The next step in the microemulsion experiments is to begin including other additives into the MCPU mixture. The first additive will likely be a surfactant designed to form closed-cell foams. Later we will also include pentane rather than chlorobenzene as a blowing agent. The advantage of pentane is that it can help generate a foam even at room temperature. However, the current reaction conditions currently require temperatures above its boiling point. We may have to therefore substitute butanediol with diaminobutane, and run the reaction at a lower temperature.

The electroless zinc protocol has so far failed to produce zinc coatings. This preparation likely required the use of a buffer. In addition, other modifications may be necessary due to the fact that the recipe was designed for nickel-zinc alloys rather than pure zinc. Another possibility may be to use nickel-zinc instead. Also popular for protecting steel, nickel-zinc is sufficiently electronegative to provide cathodic protection. Our recipe is currently optimized for creating Ni-Zn with Ni in the range of 70-80%.